NAS 9-12247

DYNATECH CORPORATION

DEVELOPMENT OF SELF EXTINGUISHING DURETTE AND/OR NOMEX FABRIC

- Final Report -

June 20, 1972

Prepared for:

Crew Equipment Branch
NASA Manned Spacecraft Center
Houston, Texas 77058

Contract NAS 9 12247
Dynatech Contract NAS 49
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Progress through Research

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Progress through Research

FOREWORD

The research described herein was conducted by the Dynatech R/D Company of Cambridge, Massachusetts under NASA Contract NAS-9-12247. The work was done under the guidance of the Technical Monitor, Mr. Jack Naimer, Crew Equipment Branch, NASA Manned Spacecraft Center. Mr. Glenn K. Armstrong of Dynatech served as project manager.

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ABSTRACT

The objective of the research performed under Contract NAS-9-12247 was to develop a treatment for "Nomex" or "Durette" fabric which would render it self extinguishing in a 70% oxygen, 30% nitrogen atmosphere at 5 psia. The treatment should not degrade excessively the physical and textile properties of the fabric and should not outgas or have an objectional odor. In addition, it was desirable that the treatment be permanent and not lose its fire protecting qualities after laundering.

A treatment which meets these requirements was developed as a result of this contractual effort. The treatment utilizes a mixture of formaldehyde, phosphorous acid and tri methyl phosphate in methanol. The cloth to be treated is held in a boiling solution of the above reagents for 24 hours, removed, air dried and then heated to 120° C in a circulating air oven for 90 minutes. The treatment turns "Nomex" a pale yellow but does not have an appreciable effect on drape or hand. One inch wide strips of treated cloth failed in tension at 192 lbs while untreated controls broke at 215 lbs. To remove any excess reagents, the cloth is processed in a home laundry through one wash and dry cycle without the use of any detergents. The LOI after this treatment is 0.49. After two launderings using Federal Standard Test Method No. 191 the limiting oxygen index is still 0.49 compared to an LOI for untreated Nomex of 0.29.

The thermal shrinkage* of the treated material is 23% compared to a control of 40% for unwashed Stern & Stern Nomex HT 90-40.

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* Dynatech Test #24, for procedure see Appendix

DYNATECH

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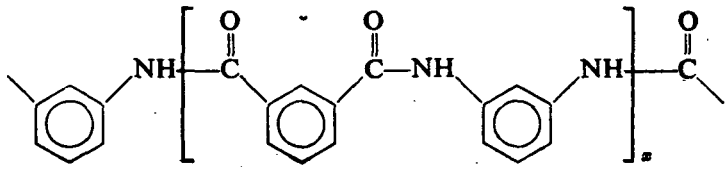
Section 1

INTRODUCTION

The voluminous literature on fire retardants indicates that incorporation of one or more of the elements P, N, Sb, Cl, Br or B into a structure will improve flame resistance. Of the single elements, phosphorous is usually the most effective at low weight additions, followed by bromine, which is superior to chlorine. Of the combinations of several elements, phosphorous and antimony reduce the amount of halogen necessary for a given level of retardance and phosphorous-bromine combinations are probably the most effective fire retardants known.

The basic polymeric substance that was used in this investigation was an aromatic polyamide believed to have the following structure:



Known by the trade name of "Nomex" and manufactured by the E.I. duPont Company, when fabric manufactured from this polymer is subjected to a patented vapor phase treatment utilizing halogens and phosphorous, it is converted into a material known as Durette which is marketed by Monsanto Corporation. The objective of this contract was to modify fabrics woven from either of these materials so they would self extinguish in a 70% O_2, 30% N_2 atmosphere at 5 psia total pressure.

A chemical process utilizing a chemical reaction with the fabric surface was believed to offer the most promise for decreasing fabric flammability while having only a minimal effect on drape, hand and other desirable fabric properties. Various reagents are known which will react with Nomex. For example, one of the most reactive points of attack on the polymer chain is the amide hydrogen. Bromine and chlorine will replace the amide hydrogen under relatively mild conditions, and the resulting halogenated fabric has an LOI of 0.47 - 0.48. Unfortunately, the nitrogen-halogen bonds formed are

easily hydrolyzed since one washing reduces the LOI of halogenated Nomex fabric to the untreated value of 0.29. To achieve a permanent finish it is necessary to brominate the ring structure of Nomex. A treatment which accomplishes this result was developed by Monsanto Research Corporation under contract NAS 9-8810. Examination of their results shows that a two pass treatment with phosphorous oxyhalide and bromide vapor for approximately 1/2 hour per pass at 365° - 380° C gave fabrics with enhanced ignition resistance. Typical weight increases after scouring were 4.43% Br, 0.13% Cl and 0.65% P. This harsh treatment degrades the tensile strength and leaves the fabric a golden brown color, but the treatment is permanent and the halogen is not removed by repeated washings. Fabrics treated in this manner have an LOI of 0.36.

The severity of the conditions which are necessary to add bromine to the ring indicate that it will be difficult to devise treatments which attach other elements to the ring atoms.

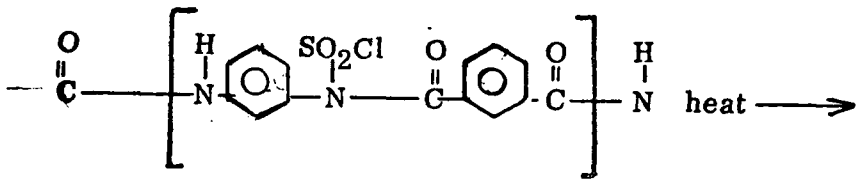
Also, the surface of fibers treated by vapor phase bromination and/or oxidative thermal treatment are "case hardened" and the treatment, used to produce Durette also produces a "case hardened" fiber and makes the fabric less reactive than the untreated Nomex. This is a serious problem if additional chemical manipulation of the Durette fabric is necessary to enhance its fire retardency. For these reasons both Nomex and Durette were selected as candidate polymers for this investigation.

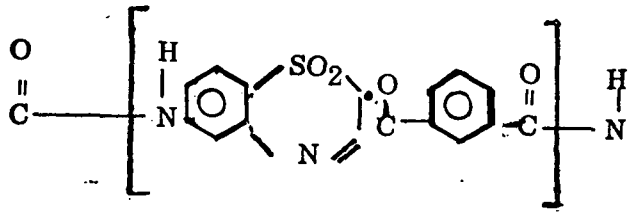
Four different reagent systems were evaluated as possible fire retardant treatments. These were:

- Chlorosulfonation
- Phosphoric acid (polyphosphoric acid) followed by heat treatment
- Tetrakis (hydroxy methyl) phosphonium chloride (THPC)
- Formaldehyde and various trivalent phosphrous compounds.

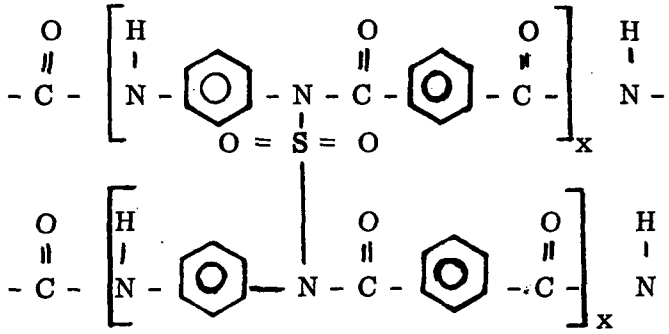
Chlorosulfonation

It is hypothesized that chlorosulfonic acid adds to the amide nitrogen but undergoes a cyclization upon heat treatment as follows:





Also, since the fabric stiffens when treated, some cross linking may be occurring:



With concentrated reagents, the carbon-nitrogen bond is undoubtedly severed since all textile properties are lost and the polymer dissolves.

The sulfonate group is not noted for being an efficient fire retardant moiety but the agressive nature of chlorosulfonic acid and the favorable reaction kinetics suggested its possible application via secondary reactions.

Phosphoric Acid

Phosphoric acid will add to Nomex and Durette under relatively mild conditions and it is effective in raising the LOI to 0.40 - 0.45. The phosphate group is easily hydrolyzed and a five minute soak in water will completely remove the effect of the treatment. Previous work at Dynatech R/D Company with other phosphoric acid treated fabrics had indicated that a very carefully controlled post heat treatment in air was beneficial in reducing water sensitivity. Thus, post heat treatment was investigated as a possible means of imparting a permanent increase in LOI to Nomex and Durette fabrics.

THPC Treatments

The commercial availability and acceptance of THPC as a fire retardant suggested its application to Nomex and Durette. Rather than apply THPC as a coating, direct reaction with the fiber appeared to be possible via the amide hydrogen. The work performed under this contract was aimed at discovering the best reaction conditions for direct addition of THPC to Nomex.

Organophosphonates and Formaldehyde

Phosphonates contain one carbon-phosphorous bond. A number of workers have concluded that fire retardant systems based on organophosphonates are very promising because of their stability, ease of synthesis, low toxicity and potential low cost. Fields* (1) in 1952 described a very facile reaction between formaldehyde, diethyl phosphite and diethylamine.

$$CH_2O + (C_2H_5)_2NH + H\overset{\nearrow O}{P} - (OC_2H_5)_2 \longrightarrow$$

$$(C_2H_5)_2NCH_2\overset{\nearrow O}{P} - (OC_2H_5)_2 + H_2O$$

* E.K. Fields, J. Am. Chem. Soc. 74, 1528 (1952).

Phosphorous Pentachloride

Nomex treated with this reagent had an LOI of 0.47 but this was reduced by washing to 0.29. In an effort to make the phosphorous more resistant to hydrolysis, 3 samples were soaked in methanol, ethanol and butanol and then heat treated. After washing all the samples had an LOI of 0.29. It was concluded that the basic phosphorous nitrogen bond was being hydrolyzed and the presence of up to four carbon atoms in the ester did not reduce the rate of hydrolysis to any appreciable extent.

The amide hydrogen on Nomex should be reactive enough to enter into this reaction, and it offers an attractive route for the addition of a hydrolysis resistant C-P bond to Nomex. As an alternative, a C-P bond may be formed via a Michaelis-Arbuzov reaction, for example, where a phosphite reacts with a halide to give

$$(RO)_3\,P + R'X \longrightarrow (RO)_2 - \overset{O}{\overset{\uparrow}{P}} - R' + RX$$

The ring bromine atoms in Durette can serve as the halide atom but probably will be quite unreactive towards phosphites. Although the amide hydrogen in Nomex can be replaced by chlorine or bromine, the reactivity of a phosphite with a halide in this position was not known. In selecting suitable reagents for this reaction availability, cost, and reactivity were considered. The principal reactants evaluated were

$$PCl_3,\ CH_3OH,\ CH_2O,\ (CH_3O)_3\,P,\ H_3PO_3,\ \text{and}\ C_2H_4O$$

Miscellaneous Reagents

Several other treatments for Nomex were evaluated to determine whether they would be effective in raising the LOI, these were:

Silicon-Tetra Chloride

Nomex was refluxed for 48 hours in a solution of 5% $SiCl_4$ in $POCl_3$, padded dry and heat treated for 1 hour in 120° C oven. The very white soft samples resulting were tested for LOI before and after washing giving values of 0.48 and 0.32 respectively.

Tri phenyl Borate

Refluxing Nomex with tri phenyl borate for 30 minutes and then heat treating @ 200° C for 5 minutes gave a sample with an LOI of 0.45. After washing this was reduced to 0.32.

Section 2

RESULTS

Samples of Durette and Nomex fabric were immersed in beakers containing various concentrations of chlorosulfonic acid. The beakers were heated on a thermostatically controlled hot plate to various temperatures and the fabric samples were immersed in the hot reagent for controlled periods of time. The temperature of the treating solution was measured with a calibrated mercury-in-glass thermometer. After treatment the samples were padded dry and then post heat treated in a circulating air oven.

Practical grade chlorosulfonic acid was obtained from duPont and was mixed either with reagent grade chloroform or phosphorous oxychloride as the diluent. For the phosphoric acid treatments, the procedure was similar and reagent grade chemicals were used.

Tables one and two summarize the results of these treatments both on Nomex and Durette. Chlorosulfonic acid is a very aggressive reagent toward Nomex or Durette and 7-12% weight additions can be achieved at room temperature with a 20 second dip in a 10% solution of the acid in chloroform. This treatment stabilized Nomex during thermal treatment but does not give a permanent increase in LOI when treated samples are laundered.

Sulfonation of the ring is preferred when chlorosulfonic acid is used in a non polar solvent such as chloroform whereas attack at the amide hydrogen is more likely when the reagent is used in a polar solvent such as phosphorous oxychloride. To determine if either method of sulfonation would give hydrolysis resistant structures, a sample of Nomex was sulfonated in a 5% solution of chlorosulfonic acid in $POCl_3$ @ 50° C for 5 minutes, heat treated 100° C for 20 minutes and then refluxed with methanol for 24 hours. The initial weight gain after sulfonation was 7.6% which was completely lost after refluxing. The LOI after chlorosulfonation was 0.43 but was

reduced to 0.29 after the methanol treatment. Similar results were observed when the sulfonation was carried out in chloroform. Also, subsequent experiments where THPC was reacted with both sulfonated and unsulfonated Nomex did not yield a great difference in weight addition between the two samples and the LOI of the final treated fabrics did not differ by more than three to five hundredths of a point. These results indicate that the sulfonated polymer is no more reactive than the unsulfonated polymer towards this reagent.

The optimum treatment for Durette which is not degrading requires a chlorosulfonic acid concentration of 5% in $POCl_3$, the mixture being heated to 100° C and the cloth immersed for 1 minute followed by a post heat treatment in an air oven at 135° C for 5 minutes. This treatment reduced the thermal shrinkage from 18% to 14% and raises the LOI from 0.35 to 0.38.

With Nomex, the chlorosulfonic treatment produces a dramatic increase in thermal stability but with no concomitant increase in LOI.

Phosphoric acid treatment without a post heat treatment actually lowers the LOI of Nomex. A 35 minute treatment in boiling acid followed by oven curing at a temperature below 130° C produced a fabric with an LOI value which was only slightly better than the control. When higher curing temperatures were used the fabric was discolored and lost tensile strength but a permanent increase in LOI was noted.

The treatment given Nomex to convert it to Durette, produces a fabric with only 18% thermal shrinkage and an LOI of 0.35. Post treatment of Durette with phosphoric acid and phosphoric acid-phosphorous pentoxide mixtures reduces the thermal shrinkage to 11-12% and raised the LOI to 0.40. However the best LOI values were obtained for the most severe treatment conditions at 200° C where some loss in tensile strength was observed. For both fabrics, permanent increases in LOI are obtained at the expense of strength, which eliminates the process as a practical means for enhancing fire retardancy.

TABLE 1 - TREATMENT OF DURETTE

Treatment Conditions			Post Heat Treatment		Observations	LOI		Thermal * Shrinkage (1)
Conc of reagent	Temp. ° C	Time min.	Temp. ° C	Time min.		before washing	after 1 wash	after 1 wash
Control						.35	.35	18
85% Phosphoric Acid	20	5	200	180			.36	11
	20	30	200	180			.36	11
	45	5	200	180			.36	--
	60	5	200	180			.36	--
	110	5	200	10	darkens		.36	--
	110	5	190	5	darkens		.36	11
	110	5	130	10	slightly dark		.36	13
	110	5	70	10	no discoloration		.36	15
	110	5	none	---				18
	132	15					.36	
150gm 85% H_3PO_4 + 50gm P_2O_5	110	60	200	10	darkens	.38	.37	12
	110	120	200	10	tenderized	.39	.39	--
	150	180	---	---	"	.40	.39	--
	200	5	---	---	tenderized		.38	--
	200	10	200	10	not tenderized but 25% loss in tensile over control (2)		.40	--
	200	15	200	10			.40	--

TABLE 1 - (continued)

Treatment Conditions			Post Heat Treatment		Observations	LOI		Thermal* Shrinkage (1)
Conc of reagent conc vol %	Temp. ° C	Time min.	Temp. ° C	Time min.		before washing	after 1 wash	after 1 wash %
Chlorosulfonic acid in phosphorus oxychloride								
100	25	2	---	---	fabric dissolved	--	---	--
20	25	5	---	---	stiff tenderized	--	---	--
	25	2	---	---		--	.41	--
	25	1	200	20		.46	.34	--
5	40	5	---	---			.35	--
	40		200	20	darkens		.34	--
10	50			---			.34	--
	70		125	20			.36	--
	70		100	20			.34	--
	90		100	20			.34	--
	100		100	20			.34	--
	100		125	20			.35	--
	100		200	20			.38	--
	100	1	135	5	5 wt % add on		.38	14
Control	---	-	---	---		.35	.35	18

(1) For test procedure see appendix

(2) non standard 1/2" x 2" samples used - results are primarily useful for comparison purposes.

TABLE II - NOMEX (HT90-40 Stern and Stern)

Treatment Conditions			Post Heat Treatment		Observation	LOI		Thermal Shrinkage	
Conc of reagent	Temp. °C	Time min.	Temp. °C	Time min.		before washing	after 1 wash	before washing	1 was
Control			---	---			.29	40	61
85% Phosphoric	25	10	---	---					
	120	20	---	---			.26		
	120	20	70	20			.26		
	120	20	130	20	grey streaks on fabric		.26		
	120	20	200	20	blacken fabric-tenderized		.45		25
	120	35	120	5		.45	.30	32	
chlorosulfonic acid in phosphorus oxychloride									
100	25	1			fabric dissolved	---	---	--	--
20	25	5	100	5	fabric stiff	.37	---	--	--
6.6	55	5	120	10	slightly stiff	---	0.29		23

THPC Tetrakis (Hydroxy methyl) Phosphonium Chloride Treatments

Four inch square samples of Nomex or Durette were placed in 300ml boiling flasks fitted with a ground glass water cooled condenser. The flasks were equipped with heating mantles and the boiling and reflux rate adjusted to several cc a minute with a variable transformer which controlled the heat input. After treatment with the refluxing mixture, the samples were padded dry, washed several times in solvent (usually DMF) and then cured in an air oven. The THPC used was an 80% solution from Hooker Chemical Co., lot 0411 and this was diluted with either reagent grade NMP (n-methyl-2-pyrrolidone) or DMF (N, N-dimethyl formamide). These reagents swell Nomex and were chosen to aid the penetration of THPC into the center of the fibers. It was also discovered that there is a heat of mixing effect with THPC and DMF or NMP. If 50 ml of THPC is mixed with 50 ml of either NMP or DMF in a 100 ml beaker the temperature rises from 25° C to 50° C. It was not determined if any reaction occurred between these reagents.

Table 3 lists the results of treatments of Durette and Nomex with THPC. Examination of this table shows that the post heat treatment step is a critical factor in achieving a permanent increase in LOI. A two minute soak followed by a 200° C post heat treatment raises the LOI to 0.39. However, this gives a very harsh fabric and heat treatment above 130° C appears to degrade the tensile strength of Nomex. Thus various mixtures of THPC and NMP and DMF were tried and post heat treatment temperatures were limited to 120° C.

In general there is a rapid initial gain in LOI during treatment. Longer treatment times produce a more permanent treatment and the LOI appears to reach a limiting value of 0.42-0.43 after scouring. The LOI of Durette is also increased by THPC treatment and the best value obtained was 0.49. The THPC treatment is effective in raising the LOI of Nomex and if carried out under nitrogen a white fabric results. The treatment does produce some increased harshness and stiffness in the fabric and if high LOI values are not required it is an effective treatment for increasing the fire retardance of Nomex.

TABLE 3

Tetrakis (Hydroxymethyl) Phosphonium Chloride (THPC) Treatments of Nomex

Reagent Conc. by Volume	Time of Treatment	Treatment Temperature	Post Heat Treatment Conditions	Scoured Once	LOI	Remarks
80% THPC	2 minutes	room temp soak	200° C 2 minutes	yes	0.39	Yellow
" "	45 minutes	reflux-air	120° C 4 hours	yes	0.34	Yellow
" "	4 hours	reflux-air	120° C 8 hours	yes	0.34	Yellow
" "	8 hours	reflux-air	120° C 15 minutes	no	0.44	Yellow
" "	8 hours	reflux-N_2	120° C 15 minutes	no	0.44	White
" "	24 hours	reflux-N_2	---	--	----	Dissolved
50 DMF	18 hours	reflux-air	120° C 15 minutes	no	0.44	
	24 hours	room temp soak	120° C 20 minutes	no	0.45	
50 THPC (80%)	24 hours	reflux-air	120° C 8 hours	no	0.47	Yellow
	24 hours	reflux-air	120° C 8 hours	no	0.49	Durette
	24 hours	reflux-N_2	120° C 5minutes	no	0.46	White
	24 hours	reflux-air	120° C 5 minutes	yes	0.43	
	24 hours	reflux-air	120° C 5 minutes	no	0.45	Sulfonated Sample
	120 hours	reflux-air	120° C 4 hours	yes	0.42	Yellow
	120 hours	reflux-N_2	120° C 4 hours	yes	0.43	Pale Yellow
	120 hours	reflux-N_2	120° C 4 hours	yes	0.45	Durette
	120 hours	reflux-air	120° C 4 hours	yes	0.44	Durette
50 DMF	24 hours	reflux	120° C 5 minutes	no	0.45	
50 THPC (80%)	24 hours	reflux	120° C 5 minutes	no	0.48	Sulfonated Sample
4 Br_2	24 hours	reflux	120° C 5 minutes	yes	0.43	Sulfonated Sample
100 DMF 50 THPC (80% soln)	4 hours	reflux	100° C 5 minutes	yes	0.38	
20 THPC (80% soln) 20 H_2O 60 DMF	5 minutes	room temp soak	120° C 15 minutes	no	0.41	
50 THPC (80%) 50 NMP	24 hours	room temp soak	120° C 20 minutes	no	0.48	
160 THPC (80%) 90 NMP	4 hours	reflux	120° C 5 minutes	yes	0.49	Durette

TABLE 3 (Continued)

Reagent Conc. by Volume	Time of Treatment	Treatment Temperature	Post Heat Treatment Conditions	Scoured Once	LOI	Remarks
75 NMP	5 minutes	65° C	200° C 5 minutes	yes	0.31	
25 H_2O	5 minutes	90° C	200° C 20 minutes	yes	0.40	Durette
25 THPC (80%)	1 hour	90° C	200° C 5 minutes	yes	0.32	
20 THPC (80%)	5 minutes	30° C	120° C 20 minutes	no	0.33	
80 NMP	10 minutes	reflux	120° C 20 minutes	no	0.42	
" "	15 minutes	reflux	120° C 20 minutes	no	0.44	
	9 hours	reflux-N_2	120° C 20 minutes	no	0.33	Durette
	9 hours	reflux-N_2	----	--	----	Dissolved

DMF - N, N-Dimethylformamide

NMP - N-Methyl - 2 - Pyrrolidone

Organophosphonate Treatments

Preliminary attempts at formation of a N-C-P bond to the amide nitrogen of Nomex via the Michaelis-Arbuzov reaction did not result in hydrolysis resistant structures. Samples of Nomex were refluxed with a mixture of 10cc of liquid Bromine in 50ml of chloroform for 10 minutes, removed, padded dry and heated at 120° C in air for 20 minutes. These samples were then refluxed with trimethyl phosphite for 10 minutes, removed, padded dry and heated at 120° C in air for 20 minutes. After one washing the LOI was 0.32, indicating that very little hydrolysis resistant phosphorous was attached to the polymer by this process. It is possible that longer reaction times would result in a more flame proof fabric, and it is recommended that this possibility be investigated in future work.

Concurrently with the above experiment, the feasibility of using formaldehyde and a phosphite to form a phosphonate was being tested. The procedure used consisted of placing a swatch of Nomex into a refluxing mixture of triethyl phosphite and formaldehyde. After treatment, the fabric samples were washed in methanol, and heated in an air oven at 120° C for 20 minutes. Table 4 summarizes the results.

TABLE 4

Effect of Various Reaction Conditions on LOI of Nomex Treated with Trimethyl Phosphite and Formaldehyde

Sample	Composition of Treatment	Reaction Conditions and Color	Wt. Add On	LOI before washing	LOI after washing
Blank	Pure Methanol	Refluxed 48 hours (white)	0.3%	--	--
1	100 ml - methanol 50 ml - $(MeO)_3P$ 50 ml - 37% Formaldehyde Soln in water 0.5 gm KOH	Reflux 48 hours post heat treat 1 hour @ 120° C (white)		0.50	0.44
2	Durette in Same Soln as 1	Reflux 24 hours (brown)	2.7%	0.49	0.49
3	300 cc - methanol 25 cc - $(MeO)_3P$ 15 gm - paraformaldehyde .75 gm - KOH	Reflux 46 hours (white)	1.1%	0.46	0.45
4	50 cc - H_2O added to (3) above and reheated with new cloth sample	Reflux 24 hours (white)	1.1%	0.47	0.45
5	100 cc - methanol 50 cc - NMP 25 cc - $(MeO)_3P$ 15 gm - paraformaldehyde .75 gm - KOH	Reflux 46 hours (white)	7.9%	0.41	0.39
6	100 cc - methanol 50 cc - NMP 25 cc - $(MeO)_3P$ 15 cc - paraformaldehyde 5 cc - phosphorous acid (40% soln)	Reflux 46 hours (white)	7.55%	0.43	0.43
7	10 cc - additional phosphorus acid added to (6) above and reheated with new cloth sample	Reflux 23 hours (white)		0.43	0.41

TABLE 4 (Continued)

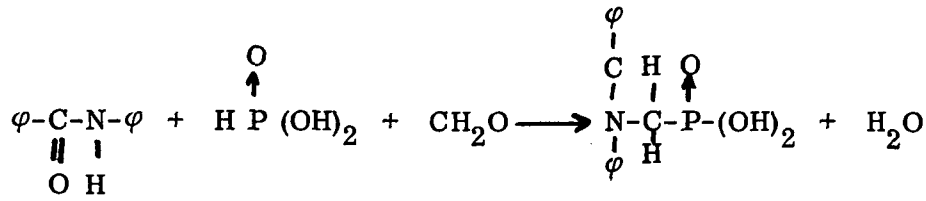
Sample	Composition of Treatment	Conditions and Color	Wt. Add On	LOI before washing	LOI after washing	Note
8	50 cc - methanol 100 cc - carbon tetrachloride 35 cc - $(MeO)_3P$ 20 gm - paraformaldehyde 3 drops Lupersol 130	Reflux 64 hrs. (white)	6.15%	0.48	0.47	passed NASA 70-30 test
9	154 cc - carbon tetrachloride 50 cc - $(MeO)_3P$ 10 gm - paraformaldehyde 2 drops Lupersol 130	Reflux 48 hours	0.6%	0.42	0.31	
10	84 cc - H_2O 40 ml - methanol 56 gm - formaldehyde 53 ml - $(MeO)_3P$ 2 gm KOH	Reflux 93 hours	5.4%	0.48		Klopman Mil Blue-Nomex 784716 (color was slightly lighter after treatment)

Trimethyl phosphite will add to Nomex both in pure methanol and in methanol with added water. The presence of NMP (as a swelling solvent) increased the weight addition but the LOI values of fabric treated this way were lower than when pure methanol was present. Later work with NMP indicated that this solvent was very difficult to remove from Nomex and the low LOI values are attributed to solvent that was not removed from the fiber. The alkaline conditions and the use of potassium hydroxide seem to be beneficial. Investigation was also made of the effect of acid conditions on trimethyl phosphite reactivity. Phosphorous acid was used in these trials but it was found to be a reactive ingredient and the results were not definitive.

The literature had indicated that carbon tetrachloride might react via a free radical mechanism with phosphites. Such a reaction would be beneficial if it occurred since it would add hydrolysis resistant chlorine to the fabric but, as shown in the table, in the absence of methanol, no permanent gain in LOI was noted. No chlorine analyses were performed on these samples but the organic peroxide and carbon tetrachloride do not serve to raise the LOI above values obtained in their absence.

A sample of royal blue Nomex poplin was refluxed in a basic solution of the phosphite in water-methanol as the solvent. This treatment had only a minor effect on the sample color and served to raise the LOI to 0.48. The outstanding characteristics of the trimethyl phosphite reaction are the absence of color, low weight add-on, and good drape and hand in the treated fabric. Further work with this system is recommended especially in the areas of reducing treatment times and in raising the LOI of scoured fabrics. Since sample 8 in the unwashed condition passed the 70-30 bottom ignition test, only a slight increase in LOI would qualify this system and would allow the treatment of predyed fabrics with only minor changes in hue after fire proofing.

Another reaction studied was the Mannich-type condensation of formaldehyde and phosphorous acid with the amide group of Nomex.



The various compositions and reaction conditions are given in Table 5. The reaction of phosphorous acid with an amine and formaldehyde has been described by Moedritzer and Irani (J. Org. Chem. 31, 1603 (1966)). This reaction apparently proceeds with the amide hydrogen of Nomex giving a N-C-P bond.

The decrease in LOI upon washing is apprently due to the ion exchange capacity of the OH groups on the acid. Refluxing with tetrabromomethane was helpful in decreasing water sensitivity but the treatment turned the fabric brown. Carrying out the reaction in methanol is beneficial since both the color of the fabric is lighter and the permanent LOI is higher. Even lighter colored fabrics were obtained by the addition of trimethyl phosphite. This combination is capable of yielding fabrics with permanent LOI's in the 0.54-0.56 range after longer treatments (48-96 hours) but the fabrics become darker yellow and lose tensile strength. The 10 sq. yard sample delivered at the completion of the contract was treated for 24 hours; (entry 9 of table 5) which represented a balance between minimum color, maximum tensile strength and adequate fire retardance.

This system appears to be catalyzed by acidic conditions but degradation of the fabric also occurs at low pH and further investigation of the effect of pH and its effect on reaction kinetics is recommended. Also the OH groups on the acid offer a convenient means of adding other substances, such as bromine to the polymer. Tetrabromomethane and 2,3-dibromopropyl alcohol were used for this purpose and the LOI after washing was 0.54 and 0.52 respectively, which represents the highest permanent LOI achieved in the program. Through further investigation of this class of reagents even higher LOI's may be possible and it is recommended that further work be done in this promising area.

TABLE 5

Phosphorous Acid - Formaldehyde Treatments of Nomex

	Reagent	Reaction Conditions Cloth Color	Add On	LOI Before Washing	LOI After One Washing
1	80 ml phosphorous acid (30% solution) 80 ml formaldehyde solution	reflux 14 hrs (yellow)	--	0.58	0.42
2	180 ml phosphorous acid (30% solution) 30 gm paraformaldehyde	reflux 18 hrs (yellow)	4.65%	0.54	--
2a	soak (2) in conc NH_4 OH for 1 hour			0.51	0.49
3	portion of (2) refluxed in tetrabromomethane	reflux 2 hrs (stained brown)	(0.3% bromo add on)	0.55	0.54
4	portion of (2) refluxed in 2, 3 dibromoalcohol	dark yellow	--	0.56	0.52
5	200 cc 30% phosphorous acid 15 cc hydrochloric acid 30 gm paraformaldehyde	dissolved some time after 24 hrs of refluxing	--	--	--
6	200 cc 30% phosphorous acid 50 cc HCl 40gm paraformaldehyde	reflux 4 hours (yellow)	13.2% (cloth was tenderized)	0.58	0.48
7	150 ml 30% phosphorous acid 80 ml 40% formaldehyde 20 gm paraformaldehyde 15 gm trichloroacetic acid	reflux 2-1/2 hrs (white)	8.9%	0.48	0.43
8	1800 cc methanol 120 gm paraformaldehyde 100 gm phosphorous acid (crystals) 1 gm KOH	reflux 54 hrs (yellow)	--	0.52	0.49
9	17000 cc methanol 454 gm phosphorous acid 500 gm paraformaldehyde 100 cc $(MeO)_3P$ 10 gm KOH	reflux 24 hrs light yellow	--	0.52	0.49

Since phosphorous trichloride and phosphorous oxychloride are readily available substances, several experiments were performed to determine whether the reaction products of these two compounds with methanol would, when refluxed with formaldehyde and Nomex, give high LOI samples. The results of these tests are given in Table 6. Entry one in the table represents the equal molar reaction:

$$PCl_3 + CH_3OH \longrightarrow CH_3O\,PCl_2 + HCl$$

The combination of the dichloride and the free HCl might be expected to dissolve Nomex after 24 hours or more of refluxing but the combination is very effective as a fire retardant and only produces a moderate loss in tensile strength as measured by a qualitative hand tearing test. However, the fabric is a bright yellow and this color may be objectional for certain applications. The exact nature of the color forming reaction both for this compound and for the phosphorous acid treatments has not been determined and should be investigated in future work. A permanent LOI of 0.41 was obtained when pentavalent phosphorous oxychloride was used. The 4.2 weight percent addition suggests that at least part of the reaction sequence does not proceed via the valency expansion step of the Michaelis-Arbuzov reaction.

TABLE 6

Coupling of Phosphites and Phosphonates to Nomex with Formaldehyde

	Reagents	Principal Reaction Product	Reaction Conditions	Add on and color	LOI Before washing	LOI After one washing
1	methanol and phosphorous trichloride	$(CH_3O)\ P\ Cl_2$	reflux 44 hrs excess formaldehyde	14.5% (yellow)	0.54	0.52
2	excess methanol and phosphorous trichloride	$(CH_3O)_2\ POH$	reflux 48 hrs in chloroform with excess formaldehyde (acidic conditions)	6.4% (yellow)	0.40	0.32
3	excess methanol and phosphorous oxychloride	$(CH_3O)_2\ P(=O)-Cl$	reflux 24 hrs under basic cond. with formaldehyde	4.2% (yellow streaks)	0.44	0.41
4	methanol and phosphorous tribromide	$(CH_3O)_2\ P\ Br$	reflux 48 hrs under alkaline cond. with formaldehyde	4.3% brown	0.53	0.49
5	ethylene oxide and phosphorous trichloride	$(ClCH_2CH_2O)_2\ P(=O)-CH_2CH_2Cl)$	reflux 48 hrs under alkaline cond. with formaldehyde	4.3% (orange)	0.33	0.31
6	ethylene oxide and phosphorous tribromide	$(BrCH_2CH_2O)_2\ P(=O)-CH_2CH_2Br$	reflux 24 hrs under acid cond. with paraformaldehyde	12.2% (brownish grey)	0.34	0.32

Section 3

CONCLUSIONS AND RECOMMENDATIONS

Chlorosulfonic acid is a very aggressive reagent towards Nomex but treated fabrics do not have a permanent increase in LOI. In addition, chlorosulfonated samples of Nomex do not possess enhanced reactivity in other selected reactions used to increase LOI. Further work with this process is not recommended.

Direct reaction of THPC with Nomex will yield a fabric with an LOI that approaches 0.43 after scouring. Durette also reacts with THPC giving a product having an LOI of 0.49. Since the range of reaction conditions investigated in this program was quite limited, it is not possible to predict if other treatments with THPC will yield higher LOI values. Some further work with this reagent appears to be justified based on the promising results obtained during these experiments.

Two very promising reactions, utilizing formaldehyde and phosphorous acid and triethyl phosphite were discovered which increase the LOI of Nomex to 0.49-0.53. Trimethyl phosphite treatment imparts no color to white fabrics and has little effect on the hue of acid dyed fabrics. Treated samples have low weight additions and are soft with good drape and hand.

Additional investigation of the reaction of trimethyl phosphite with Nomex is recommended to reduce treatment times and to determine whether higher LOI values can be obtained.

Coupling of phosphorous acid with formaldehyde to Nomex is an effective method of raising its LOI to 0.50 or above. The treatment turns white fabrics a pale yellow color. Further study of color formation during treatment is recommended since it may be possible to produce essentially white fabrics by this process. The presence of reactive groups on the phosphorous suggests that further reaction with halides or nitrogen bearing compounds will serve to decrease flammability and it is recommended that additional study be given to this possibility.

It is reasonable to suppose that such treatment may lead to fabrics with LOI values above 0.60. Of all the treatments investigated phosphorous acid-formaldehyde has the most promise for raising the flame retardance of Nomex above that achieved in this program.

APPENDIX

Test for Fabric Shrinkage During Flame Impingement

Equipment

Meker Burner-Cenco Cat. #11043
Two 2-1/4" square pieces of 40 mesh stainless steel screen
1200 ml stainless steel beaker weighing about 300 gms Fisher Cat. #2-583
4 x 4 Corning Ware Ceramic Dish (P-41 Petite Pan)
2 x 2 Steel die which cuts a sample 4.0 in^2 in area

Procedure

1. Mount the ceramic dish on a ring stand so that it is 3/8" above the Meker burner and adjust gas to give a temperature of 800° F $\pm$ 10° F as measured by a copper constantan thermocouple touching the center of the ceramic dish.
2. Place the stainless steel beaker in the hot dish for at least 2 minutes to warm.
3. Place a 2" x 2" cloth sample (A_o = 4.0 in^2) die cut from the sample to be tested between the pieces of wire screen. Remove the hot beaker and place the wire covered cloth in the hot dish and place the beaker on top. Remove after 1 min. $\pm$ 5 secs.
4. After the cloth is cool, measure area A_1 by tracing an outline on a piece of 10 x 10 per 1/2" rectangular coordinate graph paper and counting the number of squares. Calculate % shrinkage.

$$\% \text{ shrinkage} = \frac{A_o - A_1 \times 100}{A_o}$$

5. Repeat above and report the average shrinkage of the two samples.

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